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Superior photocatalytic degradation of azo dyes in aqueous solutions using $TiO_2/SrTiO_3$ nanocomposite

Loghman Karimi[1*] and Salar Zohoori[2]

Abstract

Research on photocatalytic degradation rate of azo dyes using $TiO_2/SrTiO_3$ nanocomposite in the photocatalysis process was the main goal of the present study. The $TiO_2/SrTiO_3$ nanocomposite was first synthesized under ultraviolet (UV) irradiation and sonication, and then, its photocatalytic activity has been examined under UV irradiation. The absorbance of samples was measured using a UV-vis spectrophotometer. The structure and morphology of the nanocomposite were investigated by scanning electron microscopy and the crystalline structure by X-ray diffraction spectroscopy. The results reveal that adding nano-$SrTiO_3$ to nano-TiO_2 showed the most promising photocatalytic activity toward dye degradation.

Keywords: $TiO_2/SrTiO_3$ nanocomposite, Photocatalytic degradation, Azo dyes, Irradiation, UV

Background

Environmental problem of toxic wastewater and infected waters is one of the main subjects that researchers work on. Due to this, organic dyes are one of the main industrial wastewater pollutions. More than 50% of textile dyes are azoic dyes which are recognized by their nitrogen π-bonds [1,2]. Textile and industrial dyes contain large groups of organic compounds that are produced more than 700,000 tons per year. About 1% to 20% of the world's dye products are included in the textile wastewater during the dyeing process [3-5].

The use of semiconductors such as TiO_2, ZnO, Fe_2O_3, and CdS as photocatalysts is interesting for the degradation of organic pollution. Due to the optical and electrical properties, low cost, high photocatalytic activity, chemical stability, and non-toxicity of nano-titanium dioxide, it is used as a common photocatalyst [6,7].

Although there are numerous advantages in utilizing the TiO_2, there are some disadvantages for the pure one, some of which are listed here: first, the bandgap larger than 3.2 eV causes low efficiency of nano-TiO_2. Furthermore, the electron-hole recombination rate is too high, resulting in low photocatalytic efficiency [8-11]. One of the research fields for performance improvement of TiO_2 photocatalysts is the retard of a charge recombination between excited electrons in the conduction band and holes in the valence band, which are formed by UV irradiation. Supporting the nanoparticle of a semiconductor or a metal, into which excited electrons in the conduction band of TiO_2 can be injected, is one of the methods to increase the charge separation efficiency of TiO_2 [12-15].

The perovskite oxides recognized as photocatalysts have ABO_3 formulas, where A is a rare earth metal with a large ionic radius or alkaline earth metal, and B is a transition metal with a small ionic radius. The alkali metal acts as the ionic balance (place in A) and the titanate framework plays the main role in the structure and properties with Ti in the B sites [16-19]. The presence of Sr in $SrTiO_3$ gives more ionic properties in comparison with SrO, and Ti is more covalent in $SrTiO_3$ than in TiO_2; this causes the reduction of the acidity of Ti ions and the increase of covalent property. Thus, bound formation properties might be different with titania and can lead to different photocatalitical reaction [20]. In comparison with other oxidants, the multi-cation oxide of $SrTiO_3$ is more capable of tuning the chemical and physical properties by altering the compositions and also has a larger number of photocatalytic sites [21]. By adding $SrTiO_3$ on the

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TiO_2, its demerits can be reduced. Zhang et al. produced TiO_2-$SrTiO_3$ composite heterostructures by hydrothermal treatment and proved the significant improvement in photoelectrochemical performance of TiO_2 nanotube [22].

In this study, we dedicated our efforts to synthesize photocatalysts with a better quality. The photocatalytic degradation of dark green 6 and reactive orange 72 with TiO_2/$SrTiO_3$ nanocomposite under 20- and 400-W UV irradiations is investigated. Finally, for the investigation of the TiO_2/$SrTiO_3$ nanocomposite photocatalytic efficiency, its photocatalytic activity will be compared with nano-titanium dioxide and nano-strontium titanate.

Results and discussion

Photocatalyst performance

The results acquired indicate that adding nano-$SrTiO_3$ to nano-TiO_2 particles had a tangible effect on its photocatalytic activity (Figure 1C), and its photocatalytic degradation efficiency was higher than either $SrTiO_3$ or TiO_2. When the photocatalyst is illuminated by a light with energy higher than its bandgap energy, electron-hole pairs diffuse out to the surface of the photocatalyst. At the surface, the electrons and holes can either take part in the chemical reaction with electron donors and acceptors or recombine. In the absence of suitable electron and hole scavengers, the recombination of electron-hole pairs will occur within a very short time. Therefore, observed enhancement on the photocatalytic activity of TiO_2 by supporting the $SrTiO_3$ is thought to be explained on the basis of the increase in charge separation efficiency and the excited electrons in the conduction band of TiO_2 by UV irradiation being injected to the conduction band of $SrTiO_3$ to suppress the recombination between the electrons and holes in TiO_2. In order to realize an effective suppression of the recombination, it is reasonably essential to have a contact of $SrTiO_3$ particle with TiO_2.

Particle size and surface area are the effective parameters of photocatalytic activity of nanomaterials. In our previous work, we revealed that the nano-TiO_2 has smaller particle size and higher surface area than the nano-$SrTiO_3$ [23]. Therefore, photocatalytic degradation efficiency of the nano-TiO_2 is more than the nano-$SrTiO_3$ (Figure 1A,B).

For both dark and reactive dyes, the percentage of photocatalyst degradation with a 400-W UV lamp was higher than that with 20 W. This occurs for two reasons: first of all, there is more radiation intensity, and second, there is a lower wavelength that resulted in the electron excitation of nanomaterials.

The higher degree of degradation of the reactive dye compared with the direct dye is due to the chromophore structures of the dyes, which are monoazo and trisazo, respectively [24].

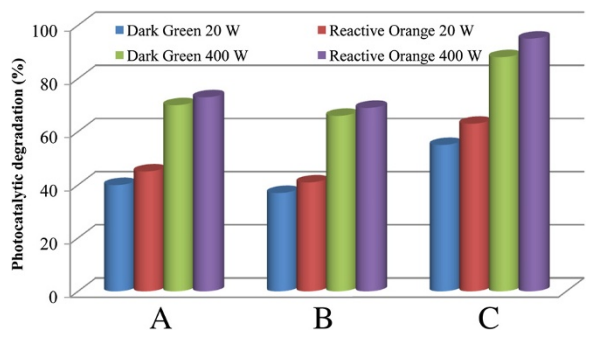

Figure 1 Photocatalytic degradation efficiency of (A) TiO_2, (B) $SrTiO_3$, and (C) TiO_2/$SrTiO_3$.

SEM-EDS measurement

A scanning electron microscopy (SEM) image (Figure 2A) provides morphological information of the TiO_2/$SrTiO_3$ nanocomposite. It is thoroughly possible to recognize the nanoparticles on the composite. It may be clearly seen that particle distribution is uniform in the TiO_2/$SrTiO_3$ nanocomposite.

Energy-dispersive X-ray spectrometry (EDS) is an analytical technique used for the elemental analysis or chemical

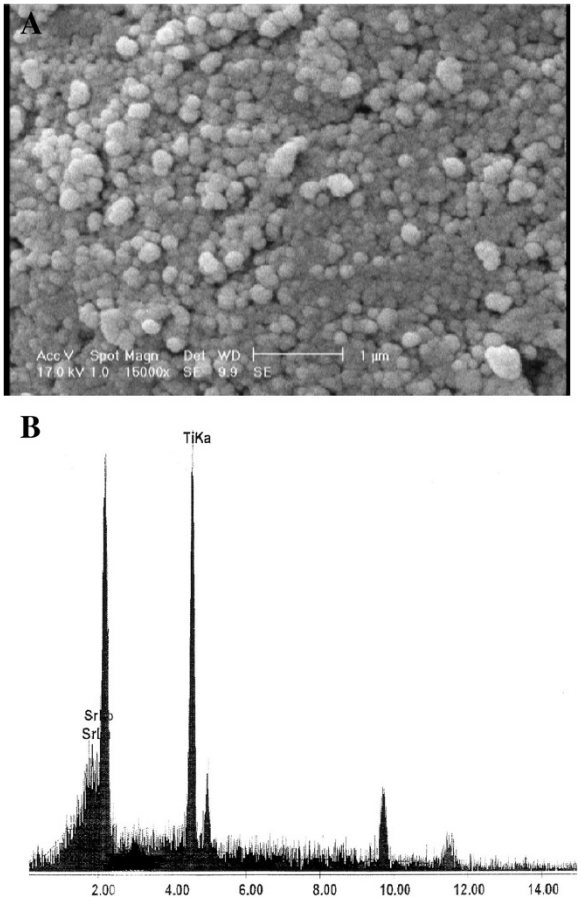

Figure 2 SEM image (A) and EDS spectrum (B) of the nanocomposite.

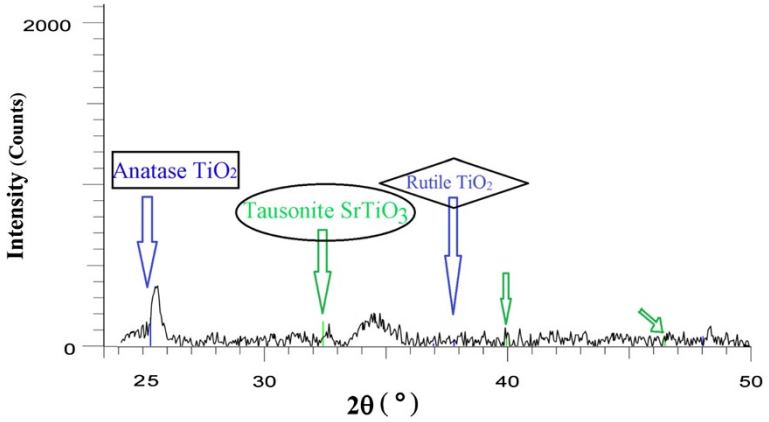

Figure 3 XRD pattern of the nanocomposite.

characterization of a sample and detects the elements using X-rays that are emitted from the specimen. Energy peaks correspond to the various elements in the sample. The presence of strontium and titanium particles on the TiO_2/$SrTiO_3$ nanocomposite was proved using EDS (Figure 2B).

XRD spectroscopy

The crystalline status of nanoparticles was studied by X-ray powder diffraction (XRD). The XRD pattern of the TiO_2/$SrTiO_3$ nanocomposite is shown in Figure 3. In the XRD pattern, the peak is around $2\Theta = 25.3°$ related to the anatase structure of nano-TiO_2, and in $2\Theta = 37.9°$, the peaks of the rutile structure of TiO_2 exist. One of the components of the fertilizing bath was $SrTiO_3$/TiO_2, as a result when the peaks of the tausonite structure of $SrTiO_3$ appeared around $2\Theta = 32.3°$. Also, the crystal size was calculated, and for the TiO_2/$SrTiO_3$, it was 201.77 Å.

Conclusion

In the present work, effective enhancement in photocatalytic activity of TiO_2 by supporting $SrTiO_3$ is experimentally confirmed. Through the XRD pattern, SEM image, and EDS spectrum, the presence of nanomaterials on the nanocomposite sample was verified. The produced nanocomposite provides a higher photocatalytic degradation efficiency in comparison with nano-strontium titanate or nano-titanium dioxide. On the composite system, strontium titanate plays the role of electron acceptor in order to accelerate photodecomposition.

Methods

Materials and equipment

Nano-strontium titanate powder (P.N.517011) with an average particle size of less than 100 nm and nano-titania (P-25) with an average particle size of about 21 nm were provided by Sigma-Aldrich (St. Louis, MO, USA) and Degussa Companies (Dusseldorf, Germany), respectively. Commercially available dark green 6 (CI 30295) and reactive orange 72 (CI 17754) were obtained from Alvan Sabet Company, Hamedan, Iran, and their structures are shown in Figure 4.

The dye solution was mixed with a magnetic stirrer during reaction (MR Hei, Heidolf, Germany). Samples after photocatalytic treatment were filtered through a Millipore filter (0.45 μm) membrane (Millipore Filter Corporation, Bedford, Massachusetts). The pH of the

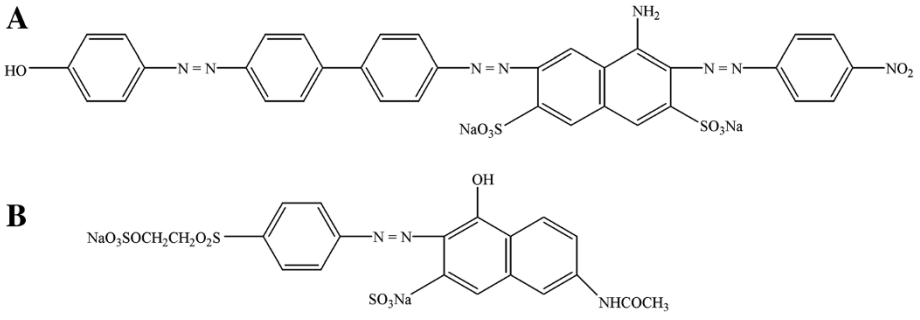

Figure 4 Structure of (A) dark green 6 (B) reactive orange 7.

solution was measured using a LI 120 pH meter (ELICO, Hyderabad, India), and concentrations of dyes were determined using a Carry 100 UV-vis spectrophotometer (Varian, Australia).

A UV-A 20W lamp (Sylvania, Belgium), with 365-nm wavelength radiation and light intensity of 0.2 to 0.4 $\mu W \cdot cm^{-2}$, and a UV400 W lamp (Philips, HPA 400 s, Guildford, England, UK), with higher radiation of wavelength between 300 and 400 nm along with the light spectrum having an intensity of 800 $\mu W \cdot cm^{-2}$ for UV-A, 115 $\mu W \cdot cm^{-2}$ for UV-B, and 25 $\mu W \cdot cm^{-2}$ for UV-C were used as light sources. An ultrasonic bath model EURONDA SPA 4D, 40 kHz (Vicenza, Italy) was used to mix the components.

SEM image and EDS spectra were obtained using a Philips XL30 scanning electron microscope (Amsterdam, Netherlands). The crystalline structure of the $TiO_2/SrTiO_3$ nanocomposite was characterized by XRD (Bruker D8 Discover X-ray diffractometer, Karlsruhe, Germany).

$TiO_2/SrTiO_3$ nanocomposite preparation

Six milligrams of nano-TiO_2 and 4 mg of nano-$SrTiO_3$ were added into 100 mL of distilled water. After 1 h of sonication and irradiation (UV-A light) of the suspension, the mixture was centrifuged and then dried at 30°C. Finally, the obtained product was calcined at 300°C for 2 h.

Procedure

The concentration of the dye in the solution was calculated by a computer program using a calibration curve. The program determines the absorbance of the dye solution at a maximum wavelength of dyes: dark green 6, 623 nm; reactive orange 72, 433 nm. The first step was the preparation of dye solution by distilled water. Then, nanomaterials were added. Firstly, the solution mixture was stirred for 15 min without irradiation in order to get equilibrium of dye adsorption. Then, the solution was irradiated with two lamps (20 and 400 W) for 1 h, and during irradiation, it was continuously stirred with a rate of 200 rpm and a temperature of 25°C, and the real dye solution pH for the direct and reactive dyes were 6.6 and 6.4, respectively. After irradiation, the samples were purified with the Millipore filter. The decolorization and photocatalytic degradation efficiency have been calculated as follows:

$$\text{Efficiency } (\%) = \frac{C_0 - C_e}{C_0} \times 100,$$

where C_0 and C_e correspond to the initial and final concentrations of the dyes before and after photo irradiation. In this equation, Efficiency % shows the dye photocatalyst degradation percent [25]. For the investigation of the $TiO_2/SrTiO_3$ nanocomposite photocatalytic efficiency, its degradation percent was compared with nano-TiO_2 and nano-$SrTiO_3$. Basic parameters were photocatalyst concentration of 0.1% (on weight of bath), 20 mg/L dye, 25°C temperature, 1 h irradiation and real pH. Figure 5 shows the schematic of dye photocatalytic degradation.

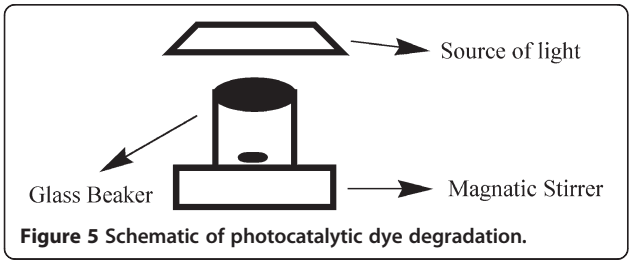

Figure 5 Schematic of photocatalytic dye degradation.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

LK participated in the idea of the study, the design of the study, interpretation of the results, and writing the manuscript for publication. SZ carried out the experiment and participated in its design, coordination, and sequence of alignments. Both authors read and approved the final manuscript.

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